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Journal
Geophysical Research Letters, 26(12)

ISSN
0094-8276

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Publication Date
1999-06-15

DOI
10.1029/1999GL900309

GEOPHYSICAL RESEARCH LETTERS, VOL. 26, NO. 12, PAGES 1699-1702, JUNE 15, 1999

Rethinking reactive halogen budgets in the midlatitude lower stratosphere

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Abstract. Current stratospheric models have difficulties in fully explaining the observed midlatitude ozone depletion in the lowermost stratosphere, particularly near the tropopause. Such models assume that only long-lived source gases provide significant contributions to the stratospheric halogen budget, while all the short-lived compounds are removed in the troposphere, the products being rained out. Here we show this assumption to be flawed. Using bromine species as an example, we show that in the lowermost stratosphere, where the observed midlatitude ozone trend maximizes, bromoform ($CHBr_3$) alone likely contributes more inorganic bromine than all the conventional long-lived sources (halons and methyl bromide) combined.

1. Introduction

While significant progress has been made in the last decade towards the understanding of mechanisms of the high-latitude ozone depletion, the reasons for the observed substantial trends of ozone in the lowermost stratosphere in the tropics and at midlatitudes [*WMO*, 1991; *McCormick et al.*, 1992; *WMO*, 1995; *SPARC*, 1998] are still the subject of heated debate. At these low altitudes, both transport and photochemistry can affect ozone, and several different interacting catalytic cycles contribute to the ozone budget. Understanding ozone chemistry in this region requires, among other things, detailed knowledge of the reactive chlorine and bromine abundances that are central players in photochemical ozone loss. In this paper, we show that current models substantially underpredict inorganic bromine (Br_y) in the lower stratosphere. Although hereafter we focus on bromine species, the principles described apply to the other halogens as well.

The importance of catalytic cycles involving bromine for ozone depletion was first pointed out by *Wofsy et al.* [1975] and *Yung et al.* [1980]. The synergistic reaction of BrO with ClO provides an efficient path for catalytic ozone depletion at low altitudes [*WMO*, 1991; *Yung et al.*, 1980]. Although bromine is considerably less abundant in the atmosphere than is chlorine, it is much more efficient in destroying lower stratospheric ozone because under normal conditions (i.e., outside the winter/spring polar regions), about half of the bromine released from the source gases is present in reactive forms (Br and BrO), compared to only a few percent of the reactive chlorine. Therefore, in the lowermost stratosphere the per-atom effectiveness of the ozone catalytic loss involving bromine is far greater than the catalytic loss involving chlorine.

Bromine atoms enter the atmosphere bound in various organic compounds of natural and anthropogenic origin [*Wamsley et al.*, 1998], and eventually are released by photolysis or reaction with OH. Unlike inorganic chlorine (Cl_y), natural sources provide a major contribution to the Br_y budget; however, ozone depletion due to bromine is coupled to the chlorine trend via the synergistic interaction of chlorine and bromine.

In stratospheric modeling studies it is generally assumed that only a few long-lived species - methyl bromide (CH_3Br), Halon-1211 (CF_2ClBr) and Halon-1301 (CF_3Br) - supply significant amounts of bromine to the stratosphere, whereas short-lived compounds get destroyed before they reach the stratosphere (e.g., [*WMO*, 1991; *Lary*, 1996; *Wamsley et al.*, 1998]).

Our simulations show that this logic has a serious flaw. Failure to include the shorter-lived gases such as bromoform as sources of stratospheric bromine results in an underestimation of Br_y in the lowermost stratosphere for several reasons. First, the tropical circulation, assisted by convection, is capable of pumping these gases upward fast enough so that non-negligible amounts make it to the upper troposphere and stratosphere before being chemically destroyed. Second, the surviving molecules of short-lived source gases release their bromine in the lowermost stratosphere, contrary to the more stable compounds such as methyl bromide and halons which start to fragment only higher up. Finally, as suggested by *Ko et al.* [1997], if the tropospheric lifetime of a source gas is comparable to or shorter than the Br_y washout lifetime, which is the case with $CHBr_3$, the direct supply of Br_y from the troposphere due to this gas provides a significant contribution to the lowermost stratospheric bromine budget, competing with the Br_y production within the stratosphere itself. In fact, we find that in the lowermost stratosphere, tropospheric supply is likely to be the largest source of inorganic bromine, as was anticipated by *Ko et al.* [1997].

We show below that bromoform is likely to contribute about 1 ppt Br_y at 12 km altitude at midlatitudes, where the conventional long-lived sources (methyl bromide and halons) are only able to maintain about 0.5 ppt Br_y.

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Paper number 1999GL900309.
0094-8276/99/1999GL900309$05.00

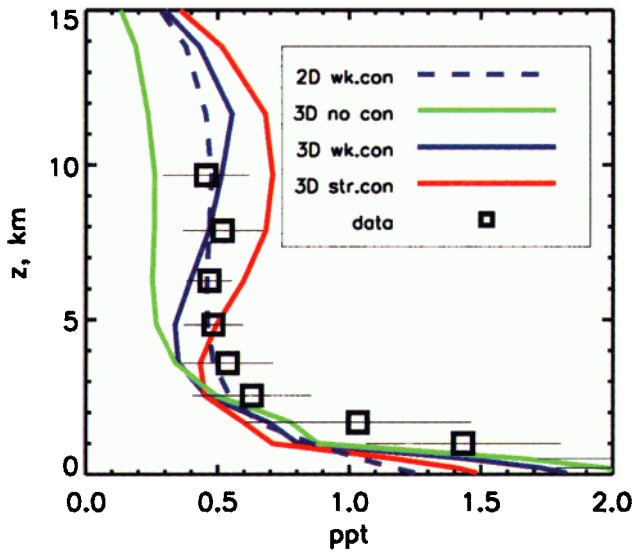

Figure 1. Height profile of $CHBr_3$ in the tropical troposphere ($\varphi = 2°S$): from PEM-T measurements, from the three 3-D simulations (without convective transport, with weak convection, and with strong convection), and from the 2-D simulation with weak convection.

2. Results and discussion

Simulations are performed with the State University of New York - St. Petersburg (SUNY-SPb) two-dimensional (2-D) model [*Smyshlyaev et al.*, 1998] with convective transport derived from the three-dimensional (3-D) NCAR Community Climate Model version 3 (CCM3) as described in [*Dvortsov et al.*, 1998]. However, in order to adjust the intensity of convection to match observations, and to set the lower boundary condition for 2-D model runs, the off-line version of CCM3 (Model of Atmospheric Transport and Chemistry (MATCH) [*Rasch et al.*, 1997]) is used to simulate the observed tropospheric distributions of bromoform and dibromomethane.

The details of the model setup can be found in [*Dvortsov*, 1998], along with a discussion of sources and sinks of bromoform and dibromomethane, briefly outlined in the following paragraphs.

Known sources of both $CHBr_3$ and CH_2Br_2 include marine macroalgae [*Moore et al.*, 1993] and phytoplankton [*Tokarczyk and Moore*, 1994]. Although a good deal of research has been done to understand the biological and physical processes controlling $CHBr_3$ and CH_2Br_2 fluxes to the atmosphere ([*Moore et al.*, 1993], and references therein), their global source strength remains largely uncertain. Thus, in 3-D experiments we vary the ocean emissions to reproduce the observed surface mixing ratios of these species. This approach allows the net global ocean-to-atmosphere fluxes to be evaluated assuming the chemical loss rates are well known. We estimate the net global flux of bromoform to have a strength of 3×10^8 kg/yr, which is consistent with the argument of *Moore et al.* [1993] that the previously reported values of 1×10^9 Kg/yr [*Penkett et al.*, 1985] and 2×10^9 Kg/yr [*Liss*, 1986] are too high. Our simulations suggest a net global flux of dibromomethane about 6.5 times smaller, amounting to 4.7×10^7 kg/yr. To our knowledge, no other global estimates of these parameters are currently available.

Bromoform is depleted primarily by photolysis in the near-UV part of the solar spectrum, while for dibromomethane the major tropospheric sink is reaction with OH, photodissociation being important only in the stratosphere. We use chemical kinetic and photochemical data recommended by [*DeMore et al.*, 1997], except for the absorption cross-sections of CH_2Br_2 where data from [*Gillotay et al.*, 1988] were used. Resulting $CHBr_3$ and CH_2Br_2 lifetimes in the tropical troposphere are of the order of 2-3 weeks and 2-3 months correspondingly, as contrasted to tropospheric lifetimes of over a year for methyl bromide and over ten years for halons.

The results of 2-D and 3-D simulations of $CHBr_3$ are presented in Figure 1, along with atmospheric observations from the Pacific Exploratory Mission - Tropics (PEM-T) campaign [*Schauffler et al.*, 1998] for one selected latitude bin in the tropics. The data clearly shows the signature of convection in bromoform height profiles, with the observed concentrations falling off with height much more slowly than predicted by the 3-D model without convective transport. Convective schemes in general, and the one employed in CCM3 [*Zhang and McFarlane*, 1995] in particular, are prone to many problems. As indicated by *Zhang and McFarlane* [1995], over the tropical oceans their convective parameterization is biased towards deep convection while underrepresenting shallow convection. Consequently, in our study the model with the original CCM3 convective transport ("strong convection") pumps about 30% too much bromoform into the upper troposphere (6-12 km) compared to observations (Figure 1) while underpredicting concentrations in the lower troposphere (below about 4 km). Since our goal is the evaluation of the stratospheric Br_y budget, we chose to adjust the convective transport to match the observed upper tropospheric distribution of $CHBr_3$. We found that to make model results agree with observations in the tropical upper troposphere, the intensity of convective transport had to be reduced to 20% of its original value ("weak convection"). Further analysis showed that the estimates of Br_y in the lowermost stratosphere are not very sensitive to the strength of convection, as discussed in detail below.

"Weak" convective mass fluxes were used to derive the parameters for driving zonally averaged convective transport as described in [*Dvortsov et al.*, 1998].

Results of the 2-D simulations are shown in Figure 1 by the dashed line. Interestingly, because the 2-D model tends to dampen deep convection in favor of shallow convection, it appears to be in better agreement with observations than the parent 3-D model.

Because dibromomethane is considerably longer-lived than bromoform, its atmospheric distribution is more zonally symmetric, and convection is of less importance. Still, comparison of 2-D and 3-D CH_2Br_2 model simulations with PEM-T data (not shown) supports the conclusions drawn from the $CHBr_3$ model-data comparison, although they are less obvious in the CH_2Br_2 case.

The large contribution of bromoform to the inorganic bromine budget in the lowermost stratosphere, the major region of interest in this study, is illustrated in Figure 2. Lower boundary conditions for the halons and methyl bromide (mixing ratios in the boundary layer) used to obtain

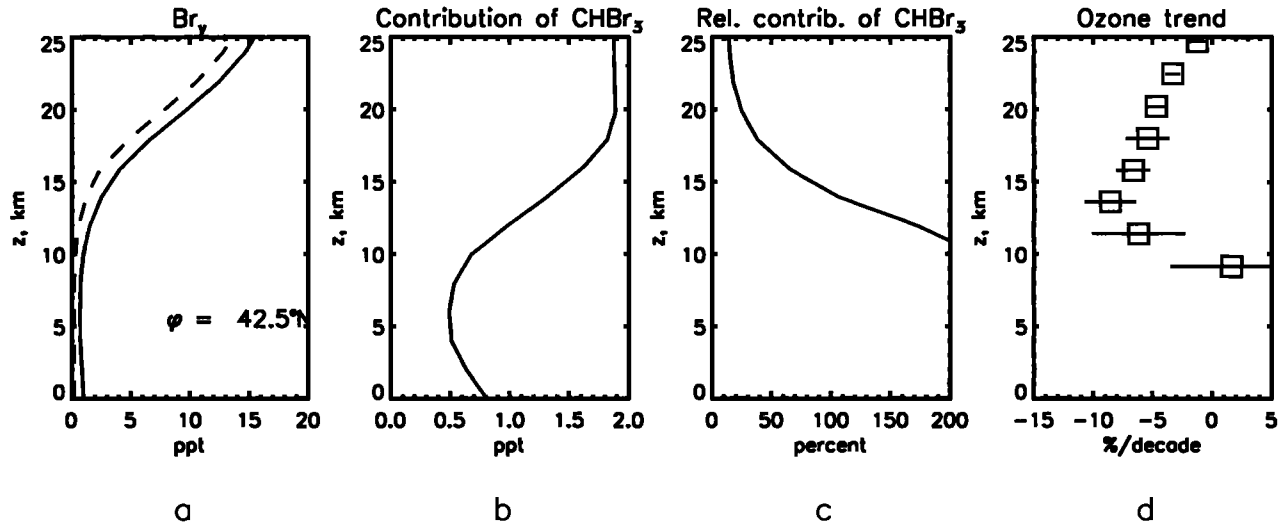

Figure 2. (a) Inorganic bromine from the 2-D model for the base run (weak convection, average tropospheric Br_y lifetime 10 days) in northern midlatitudes ($\varphi = 42.5°N$), June. Dashed line: only long-lived sources (halons and CH_3Br), solid line: long-lived sources plus $CHBr_3$; (b) contribution of $CHBr_3$, ppt; (c) relative contribution of $CHBr_3$, percent; (d) annual average ozone trend (% per decade) in northern midlatitudes [*Miller et al.*, 1995]

these results were specified according to the recommendations of [*WMO*, 1995].

Inorganic bromine is conserved throughout the stratosphere, while in the troposphere it is rained out. Unfortunately, our current ability to quantify rainout processes is very limited. Most modeling studies assume an average tropospheric lifetime of soluble species relative to rainout, τ_R, of about 10 days. We adopt the same value, along with weak convective fluxes, in our base run. The results for northern midlatitude summer are presented in panels a through c of Figure 2, while panel d shows the annual average northern midlatitude ozone trend as estimated by *Miller et al.* [1995]. Figure 2b was obtained by differencing the results of the simulation where bromoform was included as a source of inorganic bromine (shown in Figure 2a by the solid line) and the results of the model experiment where bromoform was not included (Figure 2a, dashed line), while Figure 2c shows how large (in percent) this difference is relative to the no-bromoform case.

The relative effect of adding bromoform is strongest in the lowermost stratosphere (up to about 15 km), where the long-lived sources contribute very little Br_y. For example, according to the 2-D model estimate, bromoform contributes about 1 ppt of Br_y at 12 km, which is 1.75 times more than the amount of Br_y from the long-lived sources at this height. It is quite intriguing that the observed midlatitude ozone trends maximize at the same altitudes (Figure 2d), suggesting that the extra Br_y provided by $CHBr_3$ may play an important role in the ozone depletion in this key atmospheric region.

Although the absolute contribution of $CHBr_3$ to Br_y grows with height, so do the contributions of the long-lived species, so that by ~18 km when bromoform accounts for as much as 1.9 ppt of Br_y, its share in the Br_y budget shrinks to about 30%.

According to our estimates, the effect of CH_2Br_2 is moderate compared to that of $CHBr_3$. Nevertheless, in the midlatitude lowermost stratosphere it may contribute about 40% (~0.2-0.3 ppt) extra Br_y (not shown).

The above results were obtained assuming weak convection and the rainout rates equivalent to an average tropospheric lifetime of inorganic bromine of 10 days. To test the sensitivity of our estimates to the intensities of rainout and convection, and to compare contributions of the tropospheric source (Br_y, that was produced in the troposphere, survived washout and was transported to the stratosphere) and the in-situ stratospheric source (inorganic bromine released from the source species within the stratosphere), we performed additional simulations with different specifications of convection and rainout. The results can be summarized as follows.

In the lowermost stratosphere, the model Br_y budget is dominated by the direct tropospheric source, only one quarter of which (~0.25 ppt) comes from the long-lived species, and the rest (~0.75 ppt) is from bromoform. This Br_y, produced by decomposition of bromoform within the troposphere, is transported across the tropopause by tropical upwelling, and is uniformly distributed throughout the model stratosphere. In contrast with the contribution of the tropospheric source, the contribution provided by in-situ decomposition of bromoform within the stratosphere grows with height, as does the Br_y contributed by the long-lived species, although bromoform releases its bromine at lower levels, between the tropopause and about 19 km.

This explains why Br_y estimates are not very sensitive to convection. In the region below ~15 km (where the bromoform contribution is most important), the Br_y budget is dominated by the direct tropospheric source which is practically independent of the intensity of convection. For the altitudes where differences in Br_y due to changes in the spec-

ification of model convective transport become noticeable, the total contribution of bromoform (from both tropospheric and stratospheric sources) reduces to only about 15-20%.

3. Summary and conclusions

In the present paper, we have shown that the assumption that only long-lived species can provide significant sources of stratospheric bromine (and hence deplete ozone) while short-lived compounds are harmless, is seriously flawed. It has been demonstrated that in the midlatitude lowermost stratosphere, the contribution of bromoform to Br_y is likely to be more significant than those of all the long-lived gases combined. Though bromoform is a compound of predominantly natural origin, it is linked to chlorine chemistry via a synergistic interaction between ClO and BrO, and thus is likely to play an important role in understanding the ozone photochemistry and trends in the midlatitude lowermost stratosphere. Ozone loss due to this effect will depend on the ClO abundance in this region which is uncertain at present. Based on the estimates presented in [*Wennberg et al.*, 1994, *Wennberg et al.*, 1997, and *Solomon et al.*, 1997], the additional roughly 100% increase in Br_y from bromoform as shown in Figure 2 can increase the total ozone loss rates due to the reaction of ClO + BrO below 15 km in midlatitudes by about 20 to 50 percent. Contributions from other other short-lived halogen source gases may prove to be significant as well. The detailed estimate of midlatitude ozone loss due to the contributions from bromoform and other short-lived halocarbons will be the subject of forthcoming paper.

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(Received November 20, 1998; revised February 23, 1999; accepted April 6, 1999.)